

## CHAPTER 15

### THE LAWS OF THERMODYNAMICS

#### OBJECTIVES

After studying the material of this chapter, the student should be able to:

- explain what is meant by a physical system and distinguish between an open system and a closed system.
- state the first law of thermodynamics and use this law to solve problems.
- distinguish between an isothermal process, isobaric process, isochoric process, and adiabatic process and draw a PV diagram for each process.
- calculate the work done by a gas from a PV diagram. Use the equations for an ideal gas and for the internal energy of a gas to calculate the change in internal energy of a gas and the heat added or removed during a thermodynamic process.
- calculate the amount of heat which must be added or removed to change the temperature of a gas held in a closed container under conditions of constant volume or constant pressure.
- write from memory and explain the meaning of three equivalent ways of stating the second law of thermodynamics.
- use the first and second laws of thermodynamics to solve problems involving a Carnot engine.
- distinguish between a reversible process and an irreversible process. Give examples of each type of process.
- determine the change in entropy for a system in which the thermodynamic process is either reversible or irreversible.
- distinguish between macrostate and microstate and solve problems involving the statistical interpretation of entropy.

#### KEY TERMS AND PHRASES

**thermodynamics** is the study of energy transformations in natural processes and involves relations between heat, work, and energy.

**system** is any object or sets of objects which are under consideration; everything else in the universe is called the environment. In thermodynamics, a **closed** system is one where mass may not enter or leave. In an **open** system mass may be exchanged with the environment.

**first law of thermodynamics** is a statement of the law of conservation of energy. The first law states that the change in the internal energy ( $\Delta U$ ) of a closed system is due to heat added or

removed from the system (Q) and/or work done on or by the system (W).  $\Delta U = Q - W$ .

**pressure-volume diagram** or PV diagram is used to determine the work done by a gas undergoing expansion or compression in a closed system.

**isothermal process** occurs when the temperature of the gas remains constant.

**isobaric process** occurs when the pressure is constant, the work done on or by the gas can be determined by using  $W = P \Delta V$ .

**isochoric process** occurs at constant volume,  $\Delta V = 0$ ; therefore,  $W = P \Delta V = 0$  and  $Q = \Delta U$ .

**adiabatic process** occurs when no heat flows into or out of the system. An adiabatic process usually occurs when a gas is compressed or expands so rapidly that there is no time for the heat to flow in or out of the system.

**heat engine** is a device that is capable of changing thermal energy ( $Q_H$ ), also known as the input heat or heat of combustion of the fuel, into useful work (W).

**Carnot engine** is an idealized engine where energy losses due to internal friction, turbulence present in the fuel after ignition, etc., are not considered. Carnot determined that the maximum efficiency that can be realized from a heat engine depends on the temperature of the input heat and the exhaust heat.

**refrigerators and air conditioners** operate by removing heat from a low temperature (cold) reservoir and exhausting the heat to the higher temperature (hot) reservoir. In order to accomplish this task, work is done to cause heat to travel opposite from its normal direction.

**entropy** is a quantitative measure of the disorder in a system.

**second law of thermodynamics** can be stated in several equivalent ways, three of which are:

- 1) Heat energy flows spontaneously from a hot object to a cold object but not vice versa.
- 2) It is impossible to construct a heat engine which is 100% efficient. Thus a heat engine can convert some of the input heat into useful work, but the rest must be exhausted as waste heat.
- 3) The entropy of an isolated system never decreases. It can only stay the same or increase.

## SUMMARY OF MATHEMATICAL FORMULAS

first law of thermodynamics	$\Delta U = Q - W$	The <b>first law of thermodynamics</b> is a statement of the law of conservation of energy. The first law states that the change in the internal energy ( $\Delta U$ ) of a closed system is due to heat added or removed from the system (Q) and/or work done on or by the system (W).
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heat engine	$Q_H = W + Q_L$ <p style="text-align: center;">or</p> $W = Q_H - Q_L$	A heat engine is a device that converts thermal energy ( $Q_H$ ) to useful work ( $W$ ). The heat energy not converted to useful work is ejected to the environment as exhaust heat ( $Q_L$ ).
maximum efficiency or Carnot efficiency of a heat engine	$e = W/Q_H,$ $e = (Q_H - Q_L)/Q_H$ $e = (1 - Q_L/Q_H)$ $e = (T_H - T_L)/T_H$ $e = (1 - T_L/T_H)$	The maximum efficiency or Carnot efficiency ( $e$ ) of a heat engine is equal to the ratio of the useful work ( $W$ ) to the input heat ( $Q_H$ ). The Carnot efficiency can be written in terms of the input temperature ( $T_H$ ) and the exhaust temperature ( $T_L$ ).
coefficient of performance (CP) for refrigerators or air conditioners	$CP = Q_L/W$ <p style="text-align: center;">or</p> $CP = (Q_L)/(Q_H - Q_L)$ $CP_{ideal} = (T_L)/(T_H - T_L)$	<p>The CP for a refrigerator is the ratio of the heat removed from the cold region (<math>Q_L</math>) to the work (<math>W</math>) performed to remove the heat.</p> <p>The CP for an "ideal" refrigerator in terms of the temperatures of the low temperature reservoir (<math>T_L</math>) and the high temperature reservoir (<math>T_H</math>).</p>
Entropy	$\Delta S = Q/T$	Entropy ( $S$ ) is a quantitative measure of the disorder in a system. The change in entropy ( $\Delta S$ ) for a reversible process is directly proportional to the heat ( $Q$ ) added to the system and inversely related to the temperature of the system ( $T$ ). The unit of entropy is kcal/K, where the heat is measured in kcal and $T$ in degrees Kelvin.
Statistical Interpretation of entropy	$S = k \ln W$ <p style="text-align: center;">or</p> $S = 2.3 k \log W$	The entropy of the system ( $S$ ) is proportional to the number of ways or microstates that can occur. $k = 1.38 \times 10^{-23}$ J/K (Boltzmann's constant), $\ln$ is the logarithm to the base $e$ , $e = 2.718$ , $\log$ is the logarithm to the base 10, and $W$ is the number of microstates corresponding to the given macrostate.

## CONCEPTS SUMMARY

**Thermodynamics** is the study of energy transformations in natural processes and involves relations between heat, work and energy. In this chapter we shall study the first and second laws of thermodynamics, their significance, and application.

## Physical Systems

A **system** is any object or sets of objects which are under consideration, everything else in the universe is called the environment. In thermodynamics, a **closed system** is one where mass may not enter or leave. In an **open system** mass may be exchanged with the environment.

## First Law of Thermodynamics

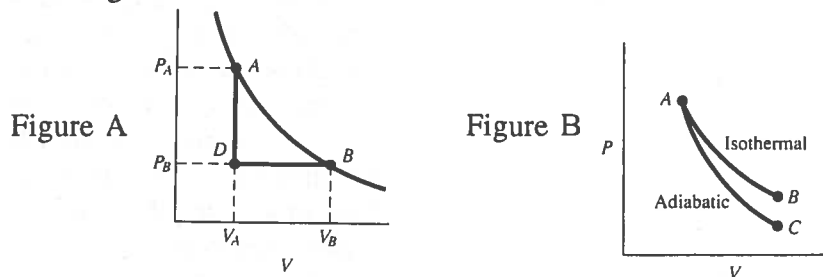
The **First Law of Thermodynamics** is a statement of the law of conservation of energy. The first law states that the change in the internal energy ( $\Delta U$ ) of a closed system is due to heat added or removed from the system ( $Q$ ) and/or work done on or by the system ( $W$ ).

$$\Delta U = Q - W$$

As a sign convention, heat added to a closed system is positive ( $Q = +$ ), while heat removed is negative ( $Q = -$ ). If work is done on the closed system, the internal energy and temperature increase and  $W$  is negative ( $W = -$ ). If an ideal gas is compressed in a cylinder with a moveable piston, the temperature and internal energy increase. If the system does work on the surroundings (environment), the ideal gas pushes the piston outward and the gas expands, the internal energy and temperature decrease and  $W$  is positive ( $W = +$ ).

## PV Diagrams

The work done by a gas undergoing expansion or compression in a closed system can be determined through use of a **pressure-volume diagram** (PV diagram). The work done during an incremental volume change ( $\Delta V$ ) equals the area under the PV curve. This area may be determined using the process of graphical integration. The following figures represent typical PV processes on an ideal gas.



In an **isothermal** process, (AB) in Fig. A, the temperature of the gas remains constant,  $\Delta U = 0$ ,  $Q = W$ . Based on the general gas law,  $PV = nRT$ , if  $n$  and  $T$  are constant, then,  $PV = \text{constant}$ .

In an **isobaric** process, (DB) in Fig. A, the pressure is constant. The work done on or by the gas can be determined by using  $W = P \Delta V$ .  $n$  and  $P$  are constant; therefore  $V/T = \text{constant}$ .

An **isochoric** process, (AD) in Fig. A, occurs at constant volume,  $\Delta V = 0$ ; therefore,  $W = P \Delta V = 0$  and  $Q = \Delta U$ . For this process,  $P/T = \text{constant}$ .

In an **adiabatic** process, (AC) in Fig. B, no heat flows into or out of the system,  $Q = 0$ , and  $W = -\Delta U$ . An adiabatic process usually occurs when a gas is compressed or expands so rapidly that there is no time for the heat to flow in or out of the system. It should be noted that an adiabatic process is quite different from an isothermal process, although the PV diagram for each process appears similar.

**TEXTBOOK QUESTION 3.** In an isothermal process, 3700 J of work is done by an ideal gas. Is this enough information to tell how much heat has been added to the system? If so, how much?

**ANSWER:** The first law of thermodynamics can be written as  $Q = \Delta U + W$ . In an isothermal process the temperature remains constant. Since the temperature remains constant, the internal energy remains constant and  $\Delta U = 0$ . Therefore, all of the heat added during the process went into the work done by the ideal gas ( $Q = W$ ). The amount of heat added to the system is 3700 J.

**EXAMPLE PROBLEM 1.** a) How much energy must be added to a 0.200 kg ice cube at 0.00°C in order to change it to water at 0.00°C. Determine b) the work done on the system during the change and c) the change in the internal energy of the system.

Part a. Step 1.  
Determine the energy required to melt the ice cube.

Solution: (Sections 15-1 and 15-2)

The ice cube is undergoing a change of phase. Use the methods of Section 14-6 to solve for the energy required to melt the ice cube.

$$Q = m \ell_f$$

$$= (0.200 \text{ kg})(80 \text{ kcal/kg})(4180 \text{ J/kcal})$$

$$Q = 6.69 \times 10^4 \text{ J}$$

Part b. Step 1.  
Determine the work done on the system during the change.

The change in volume of an ice cube when it melts is negligible. The external air pressure can be considered to be constant. Therefore,

$$W = P \Delta V$$

$$W = P (0 \text{ liters}) = 0 \text{ liter atm} = 0 \text{ joules}$$

Part c. Step 1.  
Determine the change in the internal energy of the system.

The work done on the system is zero joules; therefore, all of the heat energy added increases the internal energy of the system. However, the temperature of the system does not change during the melting process and this indicates that the increase in the internal energy cannot be in the form of kinetic energy. The increase in the internal energy is in the form of potential energy as the molecules overcome the attractive forces which hold them in the solid phase. The increase in the internal energy may be determined as follows:

$$Q = \Delta U + W$$

$$6.69 \times 10^4 \text{ J} = \Delta U + 0 \text{ J}$$

$$\Delta U = 6.69 \times 10^4 \text{ J}$$

**EXAMPLE PROBLEM 2.** One mole of an ideal gas is allowed to expand isothermally at  $-29.3^{\circ}\text{C}$  from a volume of 4.0 liters and pressure 5.0 atm to a volume of 10.0 liters and pressure 2.0 atm. a) Draw a P-V diagram for the process, b) determine the work done by the gas during the expansion.

Part a. Step 1.

The process is isothermal, i.e.,  $PV = \text{constant}$ . Complete a data table for P vs V with enough data points so that a reasonably accurate graph may be drawn.

Solution: (Section 15-2)

sample calculation

$$P_1 V_1 = P_2 V_2$$

$$(5.0 \text{ atm})(4.0 \text{ liters}) = (3.0 \text{ atm}) V_2$$

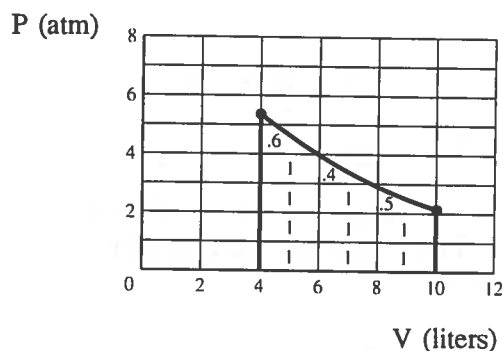
$$V_2 = 6.7 \text{ liters}$$

data table

P (atm)	V (liters)
5.0	4.0
4.0	5.0
3.0	6.7
2.0	10.0

Part a. Step 2.

Draw the PV diagram.



Part b. Step 1.

Determine the work done by the gas during the expansion.

The work done by the gas during the expansion is represented by the area under the curve between points A and B. The work done can be estimated by graphical integration, i.e., counting the complete and partial blocks under the curve and multiplying by the work represented by the area of 1 block. This method was previously used in chapter 2.

$$1.0 \text{ atm} \quad \square$$

$$2.0 \text{ liter}$$

$$\text{Work represented by one block} = (1.0 \text{ atm})(2.0 \text{ liter}) = 2.0 \text{ liter atm}$$

$$\text{sum of complete blocks} = 9.0$$

$$\text{sum of partial blocks} = 0.4 + 0.6 + 0.5 + 0.1 = 1.6$$

$$\text{Total number of blocks under the curve} = 9.0 + 1.6 = 10.6$$

work done = (10.6 blocks)(2.0 liter atm/block) = 21.2 liter atm

Because of significant figures, the answer is 21 liter atm = 2100 J.

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### *The Second Law of Thermodynamics*

The **Second Law of Thermodynamics** can be stated in several equivalent ways, three of which are:

- 1) Heat energy flows spontaneously from a hot object to a cold object but not vice versa.
- 2) It is impossible to construct a **heat engine** which is 100% efficient. Thus, a heat engine can convert some of the input heat into useful work, but the rest must be exhausted as waste heat.
- 3) The **entropy** of an isolated system never decreases. It can only stay the same or increase. If the system is not isolated, then the change in entropy of the system ( $S_s$ ) plus the change in entropy of the environment ( $S_{env}$ ) must be greater than or equal to zero. The total entropy of any system plus that of its environment increases as a result of any natural process:  
$$\Delta S = \Delta S_s + \Delta S_{env} > 0.$$

#### *First Statement of the Second Law*

The first statement of the second law is a statement from common experience. When two objects, one hot and the other cold, come into contact, heat energy will be transferred from the system at higher temperature to the system at lower temperature, but not vice versa. While the first law states that energy must be conserved, i.e., the sum of the energy lost and gained in any process must equal zero, it does not say that heat must flow from the hot object to the cold object. The first law would not be violated if the hot object became hotter while the cold object became colder. The second law states that the direction of the heat flow must be from hot to cold.

#### *Second Statement of the Second Law: Heat Engines*

A **heat engine** is a device which is capable of changing thermal energy ( $Q_H$ ), also known as the input heat or heat of combustion of the fuel, into useful work ( $W$ ). Heat engines cannot be made to be 100% efficient and while part of the heat energy is converted to useful work, the remaining heat energy will be rejected to the environment or surroundings as waste heat ( $Q_L$ ), e.g., exhaust from a car engine. Therefore,

$$Q_H = W + Q_L$$

In an idealized engine, known as a **Carnot engine**, energy losses due to internal friction, turbulence present in the fuel after ignition, etc. are not considered. Carnot determined that the maximum efficiency ( $e$ ) that could be realized from a heat engine depends on the temperature of the input heat ( $T_H$ ) and the exhaust heat ( $T_L$ ), where  $T_H$  and  $T_L$  are expressed in degrees Kelvin.

The maximum efficiency or **Carnot efficiency** of a heat engine is determined by the following formulas:

$$e = W/Q_H, \quad \text{but since } W = Q_H - Q_L, \text{ then}$$

$$e = (Q_H - Q_L)/(Q_H) \text{ and } e = (1 - Q_L/Q_H)$$

Using the input and waste heat temperatures:

$$e = (T_H - T_L)/(T_H) \text{ and } e = (1 - T_L/T_H)$$

In order for a Carnot engine to be 100% efficient, it would be necessary for the temperature of the exhaust heat to be at absolute zero (zero degrees Kelvin). This is a practical as well as a theoretical impossibility.

**EXAMPLE PROBLEM 3.** A Carnot engine takes in 3000 calories of input heat and rejects 2000 calories as waste heat. The temperature of the waste heat is 600°C. Determine the a) efficiency of the engine and b) useful work done by the engine.

<p>Part a. Step 1.</p> <p>Complete a data table based on information both given and implied in the problem.</p>	<p>Solution: (Section 15-5)</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%;"><math>Q_H = 3000 \text{ cal}</math></td> <td style="width: 50%;"><math>T_L = (600 + 273) \text{ K}</math></td> </tr> <tr> <td><math>Q_L = 2000 \text{ cal}</math></td> <td><math>e = ?</math></td> </tr> <tr> <td><math>T_H = ?</math></td> <td><math>W = ?</math></td> </tr> </table>	$Q_H = 3000 \text{ cal}$	$T_L = (600 + 273) \text{ K}$	$Q_L = 2000 \text{ cal}$	$e = ?$	$T_H = ?$	$W = ?$		
$Q_H = 3000 \text{ cal}$	$T_L = (600 + 273) \text{ K}$								
$Q_L = 2000 \text{ cal}$	$e = ?$								
$T_H = ?$	$W = ?$								
<p>Part a. Step 2.</p> <p>Determine the efficiency.</p>	$e = (Q_H - Q_L)/(Q_H)$ $= (3000 \text{ cal} - 2000 \text{ cal})/(3000 \text{ cal})$ $e = 0.333 \text{ or } 33.3 \%$								
<p>Part b. Step 1.</p> <p>Solve for the useful work done by the engine.</p>	<table style="width: 100%; border: none;"> <tr> <td style="width: 50%;"><math>e = W/Q_H</math></td> <td style="width: 50%;">alternate solution</td> </tr> <tr> <td><math>0.333 = W/3000 \text{ cal}</math></td> <td><math>W = Q_H - Q_L</math></td> </tr> <tr> <td><math>W = 1000 \text{ cal}</math></td> <td><math>= 3000 \text{ cal} - 2000 \text{ cal}</math></td> </tr> <tr> <td></td> <td><math>W = 1000 \text{ cal}</math></td> </tr> </table>	$e = W/Q_H$	alternate solution	$0.333 = W/3000 \text{ cal}$	$W = Q_H - Q_L$	$W = 1000 \text{ cal}$	$= 3000 \text{ cal} - 2000 \text{ cal}$		$W = 1000 \text{ cal}$
$e = W/Q_H$	alternate solution								
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$W = 1000 \text{ cal}$	$= 3000 \text{ cal} - 2000 \text{ cal}$								
	$W = 1000 \text{ cal}$								
<p>Part c. Step 1.</p> <p>Solve for the temperature of the input heat</p>	<p>The efficiency and temperature of the waste heat are known, therefore,</p> $e = (T_H - T_L)/(T_H)$ $0.333 = (T_H - 873 \text{ K})/T_H$ $T_H = 1310 \text{ K}$								

**EXAMPLE PROBLEM 4.** The actual work done by a heat engine in 1 hour is  $2.7 \times 10^6 \text{ J}$  while frictional losses within the engine are  $6.0 \times 10^5 \text{ J}$ . The engine operates between temperatures of 500 K and 1000 K. Determine the a) Carnot efficiency of the engine, b) number of joules of input heat taken in per hour by the engine and c) overall efficiency of the engine.



<p>Part a. Step 1.</p> <p>Complete a data table using the information both given and implied in the problem.</p>	<p>Solution: (Section 15-5)</p> $Q_H = ? \quad T_L = 500 \text{ K}$ $Q_L = ? \quad e = ?$ $T_H = 1000 \text{ K}$
<p>Part a. Step 2.</p> <p>Determine the total work done by the machine.</p>	$W_{\text{total}} = W_{\text{actual}} + W_{\text{friction}}$ $= 2.7 \times 10^6 \text{ J} + 6.0 \times 10^5 \text{ J}$ $W_{\text{total}} = 3.3 \times 10^6 \text{ J}$
<p>Part a. Step 3.</p> <p>Determine the Carnot efficiency of the engine.</p>	<p>Both the input heat temperature and waste heat temperature are known, therefore,</p> $e = (T_H - T_L)/(T_H)$ $= (1000 \text{ K} - 500 \text{ K})/1000 \text{ K}$ $e = 0.50 \text{ or } 50\%$
<p>Part b. Step 1.</p> <p>Determine the input heat per hour.</p>	<p>In order to determine the input heat, it is necessary to use the total work output during 1 hour.</p> $e = (W_{\text{total}})/(Q_H)$ $0.50 = (3.3 \times 10^6 \text{ J})/Q_H$ $Q_H = 6.6 \times 10^6 \text{ J}$
<p>Part c. Step 1.</p> <p>Determine the overall efficiency, i. e., the efficiency after frictional losses are taken into account.</p>	<p>The overall efficiency is related to the actual work done.</p> $e = (W_{\text{actual}})/(Q_H)$ $= (2.7 \times 10^6 \text{ J})/(6.6 \times 10^6 \text{ J})$ $e = 0.41 \text{ or } 41\%$

### ***Refrigerators and Air Conditioners***

Refrigerators and air conditioners operate by removing heat from a low temperature (cold) reservoir and exhausting the heat to the higher temperature (hot) reservoir. In order to accomplish this task, work is done to cause heat to travel opposite from its normal direction.

The effectiveness of a particular refrigerator or air conditioner in accomplishing the removal of heat from the low temperature reservoir is measured by the coefficient of performance (CP). The CP for a refrigerator is the ratio of the heat removed from the cold region ( $Q_L$ ) to the work

(W) performed to remove the heat, i.e.,

$$CP = (Q_L)/(W) \text{ but } W = Q_H - Q_L \text{ so that } CP = (Q_L)/(Q_H - Q_L)$$

The coefficient of performance for an "ideal" refrigerator can be written in terms of the temperature of the low temperature reservoir and the temperature of the high temperature reservoir as follows:

$$CP_{\text{ideal}} = (T_L)/(T_H - T_L)$$

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**TEXTBOOK QUESTION 7.** Can you warm the kitchen in winter by leaving the oven door open? Can you cool the kitchen on a hot summer day by leaving the refrigerator door open?

**ANSWER:** Yes, you can warm the kitchen in winter by leaving the oven door open. In the case of an electric oven, electrical energy is converted to heat energy in the heating coils. The heating coils warm the air in the oven and the warm air will warm the room. If the oven is a gas oven, the gas flame heats the air and this warm air will warm the room.

You cannot cool the kitchen on a hot summer day by leaving the refrigerator door open. A refrigerator operates by removing heat from inside the refrigerator and releasing it into the air behind the refrigerator. If the door is left open, the air in front of the refrigerator would be cooled but the air behind the refrigerator would be warmed. The additional heat generated by the compressor would cause the overall temperature of the room to increase.

The author of this study guide remembers the house of a friend where the builder had cut a hole in the kitchen wall and inserted the refrigerator. The front of the refrigerator was in the kitchen while the back portion was in the garage. Therefore, the heat generated warmed the air in the garage while the air in the kitchen was cooled.

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### ***Reversible and Irreversible Processes***

In an ideal gas, a reversible process is one in which the values of P, V, T, and U will have the same values in the reverse order if the process is returned to its original state. In this type of process, the ideal gas can be returned to its original state with no change in the magnitude of the work done or the heat exchanged. To be reversible, the process must be done very slowly, with no loss of energy due to dissipative forces such as friction and no heat conduction due to a temperature difference. In reality, these conditions cannot be met and all real processes are irreversible.

### ***Third Statement of the Second Law: Entropy***

**Entropy (S)** is a quantitative measure of the disorder in a system. The change in entropy ( $\Delta S$ ) for a reversible process is directly proportional to the heat (Q) added to the system and inversely related to the temperature of the system (T).

$$\Delta S = Q/T$$

The unit of entropy is kcal/K, where the heat is measured in kcal and T in degrees Kelvin.

The Kelvin temperature at which heat is added must remain constant for a process to be reversible.

As heat is added to a system, the average kinetic energy of the molecules increases and the motion becomes more disordered. At low temperatures we would expect to find a high degree of order while at high temperatures the system is likely to be very disordered. Thus, energy added while the system is at low temperature would introduce considerably more disorder than the same amount of energy introduced when the system is at a high temperature. Therefore, the change in entropy is inversely proportional to the temperature at which the heat is added.

### *Statistical Interpretation of Entropy*

An equivalent definition of entropy can be given from a detailed analysis of the position and velocity (i.e. microstate) of every molecule which makes up the system. The entropy of the system is proportional to the number of ways that the microstates can occur and is given by the following formula:

$$S = k \ln W = 2.3 k \log W$$

where  $k$  is Boltzmann's constant,  $k = 1.38 \times 10^{-23}$  J/K.  $\ln$  is the logarithm to the base  $e$ , where  $e = 2.718$ .  $\log$  is the logarithm to the base 10.  $W$  is the number of microstates corresponding to the given macrostate.

The state of highest entropy is the state that can be achieved in the largest number of ways and is therefore the most probable.

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**TEXTBOOK QUESTION 16.** (a) What happens if you remove the lid of a bottle containing chlorine gas? (b) Does the reverse process ever happen? Why or why not? (c) Can you think of other examples of irreversibility?

**ANSWER:** (a) Once the lid is removed, chlorine gas would gradually diffuse throughout the room. The gas molecules tend to move in random directions reaching a state of maximum disorder in agreement with the second law of thermodynamics. (b) Due to their random motions, a few molecules of chlorine gas will return to the bottle. However, the vast majority will not return to the bottle. This process is irreversible; the gas returning to the bottle would violate the second law of thermodynamics.

Another example of irreversibility would be placing 100 coins heads-up in a box and shaking the box vigorously. After shaken, there is only one way (chance) in  $1 \times 10^{29}$  that the coins could remain heads-up. The same odds apply for subsequent shaking of the box. A third example would be when a new deck of cards is opened the cards are in order according to their suit, i.e., hearts, diamonds, clubs or spades. Subsequent shuffling of the cards gives a random arrangement with high odds against ever finding the original arrangement again occurring.

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**TEXTBOOK QUESTION 19.** Suppose you collect a lot of papers strewn all over the floor; then you stack them neatly. Does this violate the second law of thermodynamics? Explain.

ANSWER: Contrary to what teenagers tell their parents, putting the papers in order does not violate the second law of thermodynamics. An outside agent, possibly the teenager but probably the parent, does work in restoring order. There is a decrease of entropy for the papers but an overall increase in entropy due to the work done by the outside agent.

**EXAMPLE PROBLEM 5.** 100 coins are placed heads up in a box. After the box is shaken vigorously, only 50 coins are found to be heads up. Determine the change in entropy of the system.

Part a. Step 1.

Determine the entropy for each macrostate.

Solution: (Section 15-10)

Based on Table 15-3 in the textbook, there is only 1.0 microstate that corresponds to the macrostate where 100 heads are found. This is because in order to have 100 heads, each coin must come up heads. However, there are  $1.0 \times 10^{29}$  microstates which correspond to the macrostate where 50 coins come up heads. The entropy for each macrostate is determined from the formula  $S = 2.3 k \log W$ .

1 head

$$S = 2.3 (1.38 \times 10^{-23} \text{ J/K}) (\log 1.0)$$

but  $\log 1.0 = 0$ ; therefore,  $S = 0$ .

50 heads

$$S = 2.3 (1.38 \times 10^{-23} \text{ J/k})(\log 1.0 \times 10^{29})$$

but  $\log 1.0 \times 10^{29} = 29$

therefore,  $S = 2.3 (1.38 \times 10^{-23} \text{ J/K})(29)$

and  $S = 9.2 \times 10^{-22} \text{ J/K}$

Part a. Step 2.

Determine the change in entropy of the universe for this process.

$$\Delta S = S_{50 \text{ heads}} - S_{100 \text{ heads}}$$

$$= 9.22 \times 10^{-22} \text{ J/K} - 0 \text{ J/K}$$

$$\Delta S = + 9.22 \times 10^{-22} \text{ J/K}$$

The change in entropy is positive, the entropy of the universe has increased in the process.

## PROBLEM SOLVING SKILLS

*For problems involving PV diagrams:*

1. Take note whether the process was isobaric, isothermic, isochoric or adiabatic.

- Use the appropriate equation(s) to complete a data table of P vs V.
- Use the data table to construct the PV diagram.
- Use the technique of graphical integration to determine the work done during the process.
- Use the ideal gas equation, the equation for the internal energy and the first law of thermodynamics to complete the solution of the problem.

For problems involving the Carnot engine:

- Complete a data table listing the input and output heat, the input and output temperatures, the efficiency, and the useful work performed.
- Use the equations involving Carnot efficiency and the first law of thermodynamics to solve the problem.

For problems related to change in entropy:

- Determine the energy added or removed from the system.
- Determine the temperature in degrees Kelvin at which the energy is added or removed.
- Use  $\Delta S = Q/T$  to determine the change in entropy.

For problems involving the statistical interpretation of entropy:

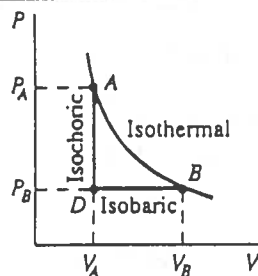
- Determine the number of microstates corresponding to the given macrostate.
- Use  $S = k \ln W = 2.3 k \log W$  to determine the entropy of the system.

## SOLUTIONS TO SELECTED TEXTBOOK PROBLEMS

**TEXTBOOK PROBLEM 5.** A 1.0 L volume of air initially at 4.5 atm of (absolute) pressure is allowed to expand isothermally until the pressure is 1.0 atm. It is then compressed at constant pressure to its initial volume and lastly is brought back to its original pressure by heating at constant volume. Draw the process on a PV diagram, including numbers and labels for the axes.

Part a. Step 1.

Draw the PV diagram and complete a data table listing the information provided.



$$P_A = 4.5 \text{ atm} \quad P_B = 1.0 \text{ atm}$$

$$V_A = 1.0 \text{ liter} \quad V_B = ? \text{ liter}$$

$$T_A = T_B \text{ (the process is isothermal)}$$

Part a. Step 2.

Use the ideal gas law to determine  $V_B$ .

$$P_A V_A = n R T_A \text{ and } P_B V_B = n R T_B$$

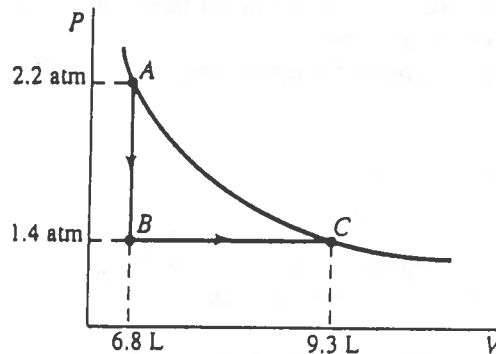
but  $n$ ,  $R$  and  $T$  remain constant; therefore,

$$P_A V_A = P_B V_B$$

$$(4.5 \text{ atm})(1.0 \text{ liter}) = (1.0 \text{ atm}) V_B$$

$$V_B = 4.5 \text{ liter}$$

**TEXTBOOK PROBLEM 10.** Consider the following two-step process. Heat is allowed to flow out of an ideal gas at constant volume so that its pressure drops from 2.2 atm to 1.4 atm. Then the gas expands at constant pressure, from a volume of 6.8 L to 9.3 L, where the temperature reaches its original value, see Fig. 15-22. Calculate (a) the total work done by the gas in the process, (b) the change in the internal energy of the gas in the process, and (c) the total heat flow into or out of the gas.



Part a. Step 1.

Calculate the total work done by the gas.

Solution: (Sections 15-1 and 15-2)

There is no change in volume between points A and B. Since  $W = P\Delta V$ , no work is done between A and B.

$$W_{\text{total}} = W_{AB} + W_{BC} \quad \text{where } W = P \Delta V$$

$$= 0 \text{ J} + (1.4 \text{ atm})(9.3 \text{ L} - 6.8 \text{ L})$$

$$W_{\text{total}} = (3.5 \text{ liter atm})(101.3 \text{ J/liter atm}) = 350 \text{ J}$$

Part b. Step 1.

Determine the change in the internal energy.

Based on the information provided in the problem, the final temperature equals the original temperature. There is no change in temperature; and therefore, there is no change in the internal energy of the gas, i. e.,  $\Delta U = 0 \text{ J}$ .

Part c. Step 1.

Determine the total heat flow into or out of the gas.

The total heat flow (Q) is given by

$$Q = W + \Delta U$$

$$Q = 350 \text{ J} + 0 \text{ J} = +350 \text{ J} \quad (\text{into the gas})$$

**TEXTBOOK PROBLEM 26.** A Carnot engine utilizes a heat source at 550°C and has an ideal (Carnot) efficiency of 28%. To increase the ideal efficiency to 35%, what must be the temperature of the heat source?

Part a. Step 1. Convert the temperature of the heat source to Kelvin.	Solution: (Section 15-5) $T(K) = T(^{\circ}C) + 273$ $T(K) = 550^{\circ}C + 273^{\circ}C = 823 K$
Part a. Step 2. Use the equation for Carnot efficiency to solve for the exhaust temperature.	$e = (T_H - T_L)/T_H$ $0.28 = (823 K - T_L)/(823 K)$ $(0.28)(823 K) = 823 K - T_L$ $230 K = 823 K - T_L$ $T_L = 593 K$
Part a. Step 3. Use the equation for Carnot efficiency to solve for the new temperature of the heat source.	$e = (T_H - T_L)/T_H$ where $e = 0.35$ $0.35 = (T_H - 593 K)/T_H$ Note: $T_L$ does not change $(0.35) T_H = T_H - 593 K$ $-0.65 T_H = -593 K$ $T_H = 910 K = 637^{\circ}C$

**TEXTBOOK PROBLEM 32.** A heat pump is used to keep a house warm at  $22^{\circ}C$ . How much work is required of the pump to deliver 2800 J of heat into the house if the outdoor temperature is (a)  $0^{\circ}C$ , and (b)  $-15^{\circ}C$ ? Assume ideal (Carnot) behavior.

Part a. Step 1. Complete a data table.	Solution: (Section 15-6) $T_L = 0^{\circ}C + 273^{\circ}C = 273 K$ $T_H = 22^{\circ}C + 273^{\circ}C = 295 K$ $Q_H = 2800 J$ $Q_L = ?$ $CP = ?$
Part a. Step 2. Determine the coefficient of performance.	Coefficient of performance (CP) for the heat pump is given by $CP = (T_H)/(T_H - T_L)$ $CP = (295 K)/(295 K - 273 K)$ $CP = 13.4$
Part a. Step 3. Determine the work performed.	$CP = Q_H/W$ $13.4 = (2800 J)/W$ $W = 210 J$

Part b. Step 1. Complete a data table.	$T_L = -15^\circ\text{C} + 273^\circ\text{C} = 258\text{ K}$ $T_H = 22^\circ\text{C} + 273^\circ\text{C} = 295\text{ K}$ $Q_H = 2800\text{ J}$ $Q_L = ?$ $CP = ?$
Part b. Step 2. Determine the coefficient of performance.	Coefficient of performance (CP) for the heat pump is given by $CP = (T_H)/(T_H - T_L)$ $CP = (295\text{ K})/(295\text{ K} - 258\text{ K}) = 7.97$
Part b. Step 3. Determine the work performed.	$CP = Q_H/W$ $7.97 = (2800\text{ J})/W$ $W = 350\text{ J}$

**TEXTBOOK PROBLEM 35.** What is the change in entropy of 250 g of steam at 100°C when it is condensed to water at 100°C?

Part a. Step 1. Determine the heat released by the steam as it changes to water.	$\Delta Q = m L_v$ Note: from Table 14-3, for water, $L_v = 22.6 \times 10^5\text{ J/kg}$ $= (250\text{ g})[(1\text{ kg})/(1000\text{ g})](-22.6 \times 10^5\text{ J/kg})$ $\Delta Q = -5.65 \times 10^5\text{ J}$ The answer is negative because heat is released by the steam.
Part a. Step 2. Determine the change in entropy.	$\Delta S = \Delta Q/T$ where $T = 100^\circ\text{C} = 373\text{ K}$ $= (-5.65 \times 10^5\text{ J})/(373\text{ K})$ $\Delta S = -1.51 \times 10^3\text{ J/K}$

**TEXTBOOK PROBLEM 41.** An aluminum rod conducts 7.50 cal/s from a heat source maintained at 240°C to a large body of water at 27°C. Determine the rate at which entropy changes per unit time in this process.

Part a. Step 1. Complete a data table.	Solution: (Section 15-7) $T_{\text{water}} = 27^\circ\text{C} + 273^\circ\text{C} = 300\text{ K}$ $T_{\text{source}} = 240^\circ\text{C} + 273^\circ\text{C} = 513\text{ K}$ $Q/t = 7.50\text{ cal/s} = 31.4\text{ J/s}$ $(\Delta S_{\text{total}})/t = ?$
Part a. Step 2. Determine the rate of change of entropy per unit time.	$(\Delta S_{\text{total}})/t = (\Delta S_{\text{source}})/t + (\Delta S_{\text{water}})/t$ but $\Delta S = Q/T$ $= (-31.4\text{ J/s})/(513\text{ K}) + (+31.4\text{ J/s})/(300\text{ K})$ $(\Delta S_{\text{total}})/t = -6.12 \times 10^{-2}\text{ J/s}\cdot\text{K} + 1.05 \times 10^{-1}\text{ J/s}\cdot\text{K} = +4.35 \times 10^{-2}\text{ J/s}\cdot\text{K}$